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Alternating Current Anodic Stripping Voltammetric Method For Trace Determination Of Thallium



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ABSTRACT

An alternating current anodic stripping voltammetric (ACASV) method has been developed for trace determination of thallium (I). The base electrolyte used is 0.05 mol L⁻¹ EDTA at which a well-defined peak is observed with E_p at -0.39 V. Parameters like concentration of maxima suppressor, pre-electrolysis time, pre-electrolysis potential, electrode dimensions, etc have been optimized. Under optimum conditions, the detection limit was found to be 0.1 µg L⁻¹ for Tl(I). The method is highly selective and sensitive and has been applied to the determination of thallium in spiked water, leaves, grapes and wine samples

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KEYWORDS

Alternating current;
Anodic stripping;
Voltammetry;
Thallium.

INTRODUCTION

The first important application of thallium was discovered in 1920 when a german company introduced a rat poison, whose active ingredient was thallium sulphate. The accidental or homicidal ingestion of thallium containing pesticides, rodenticides and depilatory agents is the major cause of exposure to humans. It is manifested by gastroenteritis, mixed neuropathy (motor and sensory), pain, vision defects and damage to the central nervous system, which may ultimately prove to be fatal. The effects have been attributed to the formation of an insoluble thal-

lium complex with riboflavin and interference with the sulphur metabolism.

Some of the analytical techniques used for the trace level determination of thallium are fluorometry^[1], FAAS^[2], spectrophotometry^[3], microtron photon activation analysis with radio chemical separation^[4] etc. Thallium has been studied polarographically by Dong et al^[5]. Applications of differential pulse anodic stripping voltammetric technique have been reported in literature^[6,7,8,9]. Complex formation with suitable ligand followed by cathodic stripping voltammetry has been reported using ligands like solochrome violet RS^[10], mandelic acid^[11] and

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cupferron^[12], xylene orange^[13].

This paper describes a very sensitive and selective alternating current anodic stripping voltammetric method for determination of thallium in real samples.

EXPERIMENTAL

Apparatus

Alternating current anodic stripping voltammetric (ACASV) studies were carried out using a Metrohm Polarecord E-506 serie-03 instrument working on 220 V stabilized AC mains. The experiments were performed in an air-conditioned room maintained at $25 \pm 1^\circ\text{C}$ and humidity 50-60%. The electrode assembly consisted of the hanging mercury drop electrode (Kemula type) as the working electrode, Ag/AgCl (sat. KCl) electrode as reference electrode and a platinum electrode as an auxiliary electrode. Nitrogen gas was used for deaeration and micropipette (25 μL) was used for addition of Tl (I) solution. Mercury was purified by aeration method followed by distillation under reduced pressure in a mercury distillation unit.

Reagents and solutions

All the chemicals used were of AR grade. The solutions were prepared in double distilled water. A stock solution of 100 ppb Tl(I) was prepared using TlNO_3 salt and desired dilutions were made as per the requirements. A 0.5M solution of EDTA and 1% solution of Triton-X 100 were prepared in double distilled water.

General procedure

In a clean dry 25 ml volumetric flask, 2.5 ml of 0.5 M EDTA and 25 μL of 1% Triton-X-100 were taken and the volume was made up to the mark with double distilled water. This was transferred to a polarographic cell and deaerated for 15 min. Pre-electrolysis was carried out with stirring and keeping the electrode potential at -0.6V for 60 sec. After a rest period of 15 sec, potential was scanned as 20 mV/s in anodic direction in AC_1 mode with frequency 75 Hz. This gave a blank voltammogram. To this solution was added 25 μL of Tl (I) solution and the voltammogram was recorded. Thallium (I) gave a well-defined symmetrical peak with an E_p value of -0.39 V. A typical voltammogram obtained for 1 μg

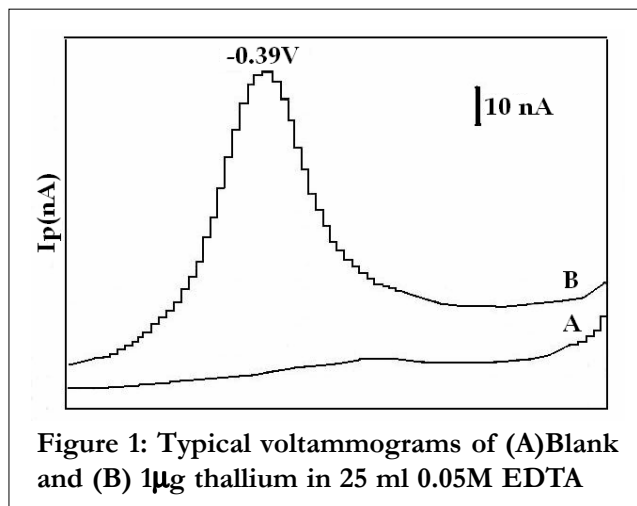


Figure 1: Typical voltammograms of (A) Blank and (B) 1 μg thallium in 25 ml 0.05M EDTA

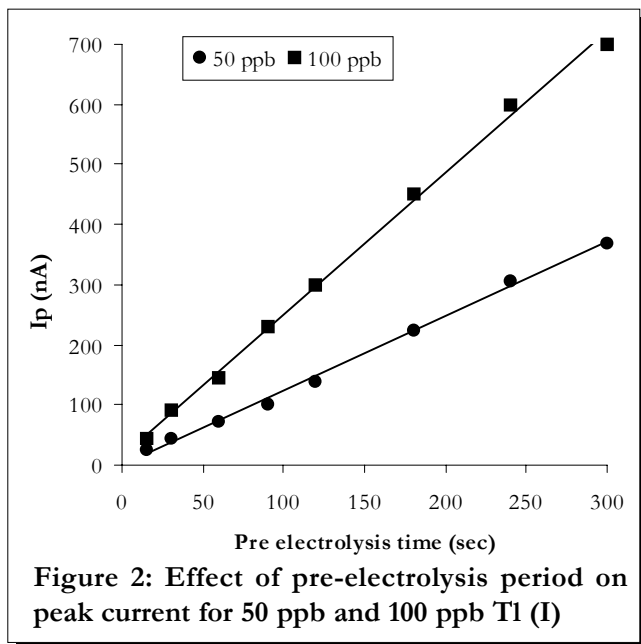
Tl(I) is shown in figure 1.

RESULTS AND DISCUSSION

AC voltammetric studies were carried out in different electrolytes like acetate buffer, EDTA, sodium citrate, HCl, NH_4Cl , etc. A symmetrical well defined peak was obtained in most of the solutions studied. There was a shift in the peak potential (E_p) in the negative direction on increasing the concentration of the electrolyte. Tl (I) gave a distinct and reproducible peak in 0.05 M EDTA with a smooth base line. Hence, EDTA was selected as supporting electrolyte for further studies.

The effect of maxima suppressors like Triton-X-100 and gelatin was studied. In presence of 0.001% Triton-X-100, the Tl(I) peak was highly symmetrical. At higher concentrations (0.01% and above), there was about 10% decrease in the peak current. Gelatin when present in a concentration of 0.001 to 0.01% did not show any change in the peak current, beyond which there was a slight decrease in the peak current (about 3%). Studies were carried out maintaining 0.001% Triton-X-100 as a maxima suppressor.

The pre-electrolysis time was varied from 15 sec to 300 sec. The current was found to increase linearly with time with no change in the E_p value (Figure 2). Pre-electrolysis time of 60 sec with a quiescent period of 15 sec was selected for further studies. The pre-electrolysis potential was varied from -0.6 V to -1.2 V. The current remained nearly con-

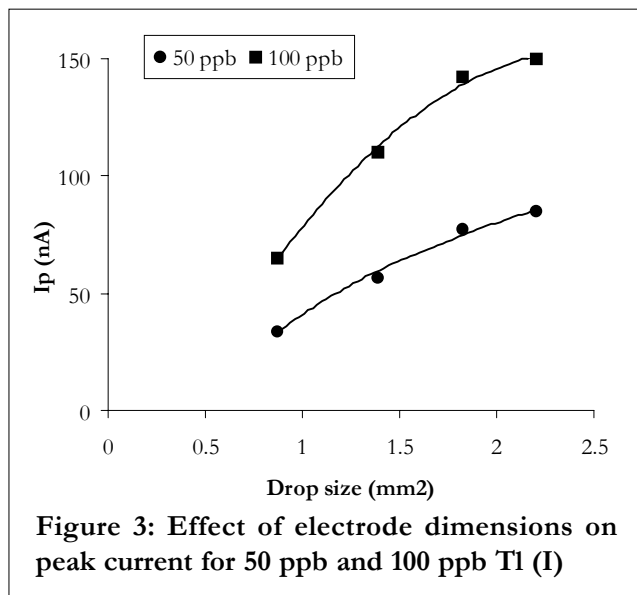


stant. A potential of -0.6 V was selected.

The effect of electrode dimension on I_p values was studied. The electrode surface was varied from 0.87mm^2 to 2.20mm^2 . An increase in drop size increased the peak current (Figure 3). Drop size of 1.82mm^2 gives a suitable well defined peak with appreciable peak current value and was maintained throughout the studies.

Dependence of current on concentration was found to be linear over the range of 0.2 to 100 ppb of Tl(I). The lowest determinable limit was 0.1 ppb. The coefficient of correlation was found to be 0.9621 and the regression equation was computed as $Y_{nA} = -0.68 + 1.49 X_{ppb}$. The values of relative mean deviation, standard deviation and coefficient of variation for 1 ppb Tl(I) were found to be 0.88% , 0.011 and 2.14% respectively. These values clearly indicate high degree of reproducibility of the method.

The effect of various ions on Tl(I) determination was studied. Their interference can be controlled by choosing different pre electrolysis potentials like -0.6 , -0.8 and -1.0 V. It was observed that the interference was minimum when pre-electrolysis was carried out at -0.6 V. The tolerance limits for various ions were found to be Pb(1:50), Cd(1:10000), Sn(1:1000), Cu (1:100), In (1:100), Ga (1:1000) and Al (1:10000). Fe(II), Ni(II), Co(II), Co(III) and Fe(III) did not interfere at all showing satisfactory selectivity of the method.



Applications

Determination of Tl(I) in spiked water samples

In three different beakers, 100 ml tap water was taken. In two beakers, aliquots containing $1.25\text{ }\mu\text{g}$ and $2.50\text{ }\mu\text{g}$ of Tl(I) solution was added while the third beaker acted as the blank. To all the beakers 2 - 3 drops of conc. HNO_3 was added and the solution was heated vigorously to reduce the volume. After cooling, liquid NH_3 was added to neutralize the solution. 2.5 ml of 0.5 M EDTA was added and maintaining 0.001% Triton-X-100 the volume was made up to 25 ml.

The voltammograms for the solutions in each beaker were recorded, corrections were made for blank and the concentration of Tl(I) estimated by standard addition method. Results obtained are presented in TABLE 1.

TABLE 1: Determination of Tl(I) in spiked water samples

Volume of tap water (ml)	Amount of Tl(I) (μg)	
	Actual	Observed*
100	1.25	1.245 ± 0.007
100	2.50	2.489 ± 0.010
200	1.25	1.242 ± 0.005
200	2.50	2.495 ± 0.013

*(Avg $\pm$ SD) of 3 observations

Determination of Tl(I) in food samples

Leafy vegetables and fruits, which are an essential part of our regular diet, may contain contami-

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TABLE 2: Determination of Tl(I) in various samples

Sample	Concentration of thallium (ng/g)	
	Present method*	AAS method
Coriander	35.84 ± 1.12	34.05
Spinach	22.96 ± 0.25	22.90
Green grapes	30.41 ± 0.36	30.06
Black grapes	23.45 ± 0.24	22.64
Wine	0.375 ± 0.012	0.34
Rum	0.20 ± 0.010	0.18

*(Avg ± SD) of 3 observations

nants. The determination of Tl(I) in coriander and spinach as well as in green and black grapes was done. For this, the samples were purchased from the local market. The wine and rum samples were purchased and analyzed for Tl(I) content.

The leaf samples and grapes were dried at 105⁰ C and powdered. 2 g each of the dried solid sample or 50 ml of the wine/ rum sample were transferred to a Kjeldahl's flask. 10 ml concentrated H₂SO₄ and 1 ml H₂O₂ (30%) was added and heated. Some more H₂O₂ was added and the heating was done very carefully. After complete dissolution of the sample, a slight excess of H₂O₂ was added and the solution was heated on a sand bath until the solution became colourless. The solution was filtered and the volume was made up to 50 ml. To this was added 1 ml conc. HBr (47%) and 2 ml 5% bromine solution. This was cooled and the solution was extracted 2-3 times with 10 ml diethyl ether. The ether extract was transferred to a beaker. To it was added 0.5 ml conc. H₂SO₄ and the ether was evaporated on a sand bath in a fume cupboard. Excess H₂SO₄ leads to the formation of Na₂SO₄, which may interfere during Thallium determination. Therefore, the concentration of H₂SO₄ used was as minimum as possible.

The residue was then treated with 2-3 drops of H₂O₂ and again heated. The solution was taken with 10-12 ml DDW and 2.5 ml of 0.5 M EDTA solution and 25 µl of 1% Triton-X-100 was added. The pH was adjusted to 4.5 – 4.8 with as little quantity of NaOH as possible. The solution was finally made up to 25 ml and the voltammograms were recorded. The actual amount of Tl(I) present in these samples was determined by standard addition method and the results obtained as an average of three determination were compared with those obtained by AAS method (TABLE 2).

CONCLUSION

A simple rapid method has been developed for the determination of Tl(I) at trace level in EDTA medium. The method was found to be reproducible, reliable and accurate. The sensitivity as well as selectivity is better than previously known methods^[7,10,12]. An important advantage of the method is that 60 s of accumulation period is sufficient to achieve the sensitivity of 0.1 µg L⁻¹. The method can be applied to wide range of samples and the results obtained are in good agreement with those obtained by AAS method.

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